



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

REC'D 23 AUG 2004

WIPO

PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03254297.9



Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

BEST AVAILABLE COPY



Anmeldung Nr:
Application no.: 03254297.9
Demande no:

Anmeldetag:
Date of filing: 07.07.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Akzo Nobel N.V.
Velperweg 76
6824 BM Arnhem
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Silyl ester copolymer compositions

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

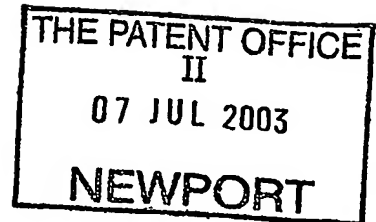
C08G77/00

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

ACO 3010 PDEP

SILYL ESTER COPOLYMER COMPOSITIONS



The present invention relates to silyl ester copolymer solutions and anti-fouling coating compositions comprising a silyl ester copolymer and an ingredient
5 having biocidal properties for aquatic organisms.

Man-made structures such as boat hulls, buoys, drilling platforms, oil production rigs, and pipes which are immersed in water are prone to fouling by aquatic organisms such as green and brown algae, barnacles, mussels, and the like.
10 Such structures are commonly of metal, but may also comprise other structural materials such as concrete or wood. This fouling is a nuisance on boat hulls, because it increases frictional resistance during movement through the water, the consequence being reduced speeds and increased fuel costs. It is a nuisance on static structures such as the legs of drilling platforms and oil
15 production rigs, firstly because the resistance of thick layers of fouling to waves and currents can cause unpredictable and potentially dangerous stresses in the structure, and, secondly, because fouling makes it difficult to inspect the structure for defects such as stress cracking and corrosion. It is a nuisance in pipes such as cooling water intakes and outlets, because the effective cross-
20 sectional area is reduced by fouling, with the consequence that flow rates are reduced.

It is known to use anti-fouling paint, for instance as a top coat on ships' hulls, to inhibit the settlement and growth of marine organisms such as barnacles and
25 algae, generally by release of a biocide for the marine organisms.

Traditionally, anti-fouling paints have comprised a relatively inert binder with a biocidal pigment that is leached from the paint. Among the binders which have been used are vinyl resins and rosin. Vinyl resins are seawater-insoluble and
30 paints based on them use a high pigment concentration so as to have contact between the pigment particles to ensure leaching. Rosin is a hard brittle resin that is very slightly soluble in seawater. Rosin-based anti-fouling paints have

ACO 3010 PDEP

2

been referred to as soluble matrix or eroding paints. The biocidal pigment is very gradually leached out of the matrix of rosin binder in use, leaving a skeletal matrix of rosin, which is washed off the hull surface to allow leaching of the biocidal pigment from deep within the paint film.

5

Many successful anti-fouling paints in recent years have been "self-polishing copolymer" paints based on a polymeric binder to which biocidal tri-organotin moieties are chemically bound and from which the biocidal moieties are gradually hydrolysed by seawater. In such binder systems, the side groups of a linear polymer unit are split off in a first step by reaction with seawater, the polymer framework that remains becoming water-soluble or water-dispersible as a result. In a second step, the water-soluble or water-dispersible framework at the surface of the paint layer on the ship is washed out or eroded. Such paint systems are described for example in GB-A-1 457 590.

15

Alternative self-polishing anti-fouling paint systems have been developed based on silyl ester copolymers. Silyl ester copolymers and anti-fouling compositions comprising these copolymers are, for example, described in WO 00/77102 A1, US 4,593,055, and US 5,436,284. Normally, a silyl ester copolymer solution is prepared which is subsequently used as one of the ingredients of the coating composition.

20

EP 0 775 733 A1 describes anti-fouling coating compositions comprising a chlorinated paraffin and a silyl ester copolymer having a weight-average molecular weight within the range of 1000 to 150,000. The viscosity of the silyl ester copolymer in solution can be between 30 and 1000 centipoise at 25 °C in a 50 weight percent xylene solution. In the examples, silyl ester copolymer solutions have been prepared with a solid content below 50 weight percent. The coating compositions prepared from these solutions comprise a high amount of volatile content. Coating compositions comprising a lower volatile content are not disclosed or suggested.

25

30

ACO 3010 PDEP

3

EP 0 802 243 A2 describes anti-fouling coating compositions comprising a silyl ester copolymer having a weight-average molecular weight within the range of 1,000 to 150,000. It is mentioned that the solid content of a solution of the silyl ester copolymer may be between 5 and 90 weight percent. In the examples, however, the prepared copolymer solutions comprise 50 weight percent volatile solvent content, and the coating compositions prepared from these solutions comprise a high amount of volatile content. It is not disclosed in this document how a high solids copolymer solution can be obtained. Further, it is not disclosed what specific properties such a high solids copolymer solution should have in case it is used to prepare an anti-fouling coating composition.

A drawback of coating compositions comprising a high amount of volatile organic compounds is that a large amount of these substances may have to be evaporated, while the volatile organic content (VOC) level is restricted by present day legislation in many countries. For example, in the United States of America federal regulations limit the content of volatile organic hazardous air-pollutants (generally synonymous with VOC) to less than 400 grams per litre for anti-fouling coatings. There is, accordingly, a need for anti-fouling coatings that comprise a lower level of volatile organic compounds, preferably having a VOC of less than 400 grams per litre.

The most common means of application of an antifouling coatings are airless spray, brush or roller. We have found that to prepare a self-polishing antifouling coating composition comprising a silyl ester copolymer and having a VOC of less than 400 grams per litre that can be applied by airless spray, brush, roller or other common application methods, it is necessary to use a silyl ester copolymer solution having a solids content of at least 55 per cent by weight and having a viscosity of 20 poise or less, preferably 10 poise or less at 25 °C; otherwise the viscosity of the coating is too high to enable satisfactory application properties, or additional solvent must be added at the point of application such that VOC limits may be exceeded.

ACO 3010 PDEP

4

Besides the above-mentioned demands on the coating composition, the resulting anti-fouling coatings on ships should have a high integrity, i.e. show almost no cracking and a good adhesion, particularly when applied to those
5 parts of a vessel where the coating is alternately wet and dry, for instance at the waterline. Further, the coating should hardly show a so-called cold flow or plastic deformation. In other words, the film should not ripple when the ship moves in the water. Additionally, the coating composition needs to show a sufficiently short drying time.

10

The present invention specifically relates to silyl ester copolymer solutions, coating compositions comprising a silyl ester copolymer, and substrates and structures having a cured coating prepared from such a coating composition. It was found that adjusting the weight-average molecular weight, the
16 polydispersity, the glass transition temperature and the amount of side chains of the silyl ester copolymer could influence the copolymer solution properties, the coating composition properties, and the coating properties.

Polydispersity (D) is defined as the ratio of the weight-average molecular weight (Mw) to the number-average molecular weight (Mn) of the polymer.

20

The present invention relates to a silyl ester copolymer solution having a solid content of at least 55 weight percent, preferably at least 60, even more preferred at least 65 weight percent, and a viscosity of less than 20 poise, preferably less than 10 poise, even more preferably less than 5 poise at 25 °C.

25 The silyl ester copolymer in solution preferably has a weight average molecular weight of more than 1500, even more preferably of more than 2000, the weight average molecular weight preferably is less than 20,000, even more preferably less than 15,000. The copolymer preferably has a polydispersity of more than 1.1; the polydispersity is preferably less than 3.0, even more preferably less
30 than 2.8. The silyl ester copolymer in solution preferably has a glass transition temperature above 5 °C, even more preferably above 10 °C; preferably the

ACO 3010 PDEP

5

glass transition temperature is below 90 °C, even more preferably below 60 °C. Preferably more than 10 weight percent, even more preferably more than 30 weight percent, and highly preferred more than 40 weight percent of said copolymer consisting of building blocks having side chains with a silyl ester
5 functionality. Preferably less than 70 weight percent, even more preferably less than 60 weight percent of said copolymer consisting of building blocks having side chains with a silyl ester functionality.

The present invention further relates to a stable anti-fouling coating composition
10 having a VOC below 400 gram per litre and a viscosity of less than 20 poise, preferably less than 10 poise, even more preferably less than 5 poise at 25 °C. Preferably the anti-fouling composition comprises:

- a silyl ester copolymer preferably having a weight average molecular weight of more than 1500, even more preferably of more than 2000, the weight
15 average molecular weight preferably preferably is less than 20,000, even more preferably less than 15,000, a polydispersity preferably of more than 1.1, preferably less than 3.0, even more preferably less than 2.8; a glass transition preferably above 5 °C, even more preferably above 10 °C; preferably the glass transition temperature is below 90 °C, even more
20 preferably below 60 °C, preferably more than 10, even more preferably more than 30, highly preferred more than 40, and preferably less than 70, even more preferably less than 60 weight percent of said silyl ester copolymer consisting of side chains having a silyl ester functionality, and
- an ingredient having biocidal properties for aquatic organisms

25

Films prepared from the coating composition according to the present invention show a good integrity and a low cold flow.

During the preparation of the coating composition, the silyl ester copolymer
30 solution is preferably added in an amount of between 1 and 60 percent by weight, more preferably between 5 and 50 percent by weight, even more

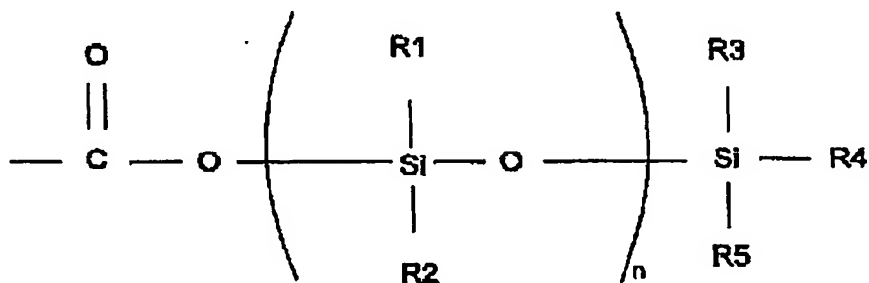
ACO 3010 PDEP

6

preferably between 15 and 45 percent by weight, based upon the total weight of the coating composition.

5 In the coating composition, the ingredient having biocidal properties for aquatic organisms preferably is present in an amount of between 0.1 and 70 percent by weight, more preferably between 1 and 60 percent by weight, even more preferably between 2 and 55 percent by weight, based upon the total weight of the coating composition.

10 The silyl ester copolymer present in the silyl ester copolymer solution and the coating composition according to the present invention is a copolymer comprising at least one side chain bearing at least one terminal group of the formula (I):



15

wherein n is 0 or an integer of 1 to 50, and R1, R2, R3, R4, and R5 are each independently selected from the group consisting of optionally substituted C₁₋₂₀-alkyl, optionally substituted C₁₋₂₀-alkoxy, optionally substituted aryl, and optionally substituted aryloxy.

20 Preferably, at least one of the groups R1-R5 in the silyl ester copolymer is methyl, isopropyl, n-butyl, isobutyl, or phenyl. More preferably, n is 0 and R3, R4, and R5 are the same or different and represent isopropyl, n-butyl, or isobutyl.

ACO 3010 PDEP

7

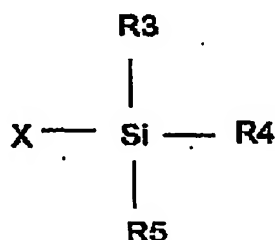
- In the present context, the term C_{1-20} -alkyl represents straight, branched, and cyclic hydrocarbon groups having from 1 to 20 carbon atoms, such as methyl, ethyl, propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, cyclohexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tertadecyl, hexadecyl, octadecyl, and icosyl. The term substituted C_{1-20} -alkoxy means C_{1-20} -alkyl oxy, such as methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, pentoxy, hexoxy, cyclohexoxy, heptoxy, octoxy, nonoxy, decoxy, undecoxy, dodecoxy, tertadecoxy, hexadecoxy, octadecoxy, and ocooxy. The term aryl is to be understood to mean an aromatic carbocyclic ring or ring system, such as phenyl, naphthyl, biphenyl, and xylyl. The term "optionally substituted" is used to indicate that the group in question may be substituted with substituents one or more times, preferably 1 to 5 times. These substituents may, for example, be hydroxy, alkyl, hydroxyalkyl, alkylcarbonyloxy, carboxy, alkoxy, alkenyloxy, oxo, alkyl-carbonyl, aryl, amino, alkylamino, carbamoyl, alkylaminocarbonyl, aminoalkyl-aminocarbonyl, aminoalkylaminocarbonyl, alkylcarbonylamine, cyano, guanidino, carbamido, alkanoyloxy, sulphonyl, alkylsulphonyloxy, nitro, sulphonyl, alkylthio, and halogen.
- 20 A silyl ester copolymer comprising at least one side chain bearing at least one terminal group of the above-described formula (I) can, for example, be obtained by copolymerising one or more vinyl polymerisable monomers with one or more monomers comprising one or more olefinic double bonds and one or more of the above-described terminal groups (I).
- 25 Examples of suitable vinyl polymerisable monomers, which can be copolymerised with one or more monomers comprising one or more olefinic double bonds and one or more of the above-described terminal groups (I), include (meth)acrylate esters such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl methacrylate, and methoxyethyl methacrylate; maleic acid esters such as dimethyl maleate and diethyl maleate; fumaric acid esters such as dimethyl fumarate and diethyl
- 30

ACO 3010 PDEP

8

fumarate; styrene, vinyl toluene, α -methyl-styrene, vinyl chloride, vinyl acetate, butadiene, acrylamide, acrylonitrile, (meth)acrylic acid, acrylic acid, isobornyl methacrylate, maleic acid, and mixtures thereof. Preferably, a mixture of methyl (meth)acrylate or ethyl (meth)acrylate with another vinyl polymerisable
 5 monomer is used. It is possible to adjust the polishing rate of the coating by using a mixture of a hydrophobic and a hydrophilic (meth)acrylate. Optionally a hydrophilic comonomer is included such as methoxy ethyl (meth)acrylate or a higher polyethylene oxide derivative, such as ethoxy ethyl (meth)acrylate, propoxy ethyl (meth)acrylate, butoxy ethyl (meth)acrylate, a polyoxyethylene
 10 glycol monoalkyl ether (meth)acrylate, such as polyoxyethylene (n=8) glycol monomethyl ether methacrylate, or N-vinyl pyrrolidone.

Examples of suitable monomers comprising one or more olefinic double bonds and one or more of the above-described terminal groups (I), which can be copolymerised with one or more vinyl polymerisable monomers, include
 15 monomers comprising one or more of the terminal groups (I) in which $n = 0$, and which may be represented by the formula (II):



wherein R3, R4, and R5 are as defined above, and X is a (meth)acryloyloxy group, a maleinoyloxy group, or a fumaroyloxy group.

20 The preparation of the monomers (II) can, for example, be performed according to the methods described in EP 0 297 505, or according to the methods described in EP 1 273 589 and the references cited therein. Examples of suitable (meth)acrylic acid-derived monomers include: trimethylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tri-n-propylsilyl (meth)acrylate,
 25 triisopropylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-tert-butylsilyl (meth)acrylate, tri-n-amylyl (meth)acrylate, tri-

ACO 3010 PDEP

9

n-hexylsilyl (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-dodecylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, tri-p-methylphenylsilyl (meth)acrylate, tribenzylsilyl (meth)acrylate, dimethylphenylsilyl (meth)acrylate, dimethylcyclohexyl (meth)acrylate, ethyldimethylsilyl (meth)acrylate, n-butyl-
6 butyldimethylsilyl (meth)acrylate, t-butyldimethylsilyl (meth)acrylate, diisopropyl-n-butylsilyl (meth)acrylate, n-octyldi-n-butylsilyl (meth)acrylate, diisopropylstearyl-
silyl (meth)acrylate, dicyclohexylphenylsilyl (meth)acrylate, t-butyl-
diphenylsilyl (meth)acrylate, and lauryldiphenylsilyl (meth)acrylate. Preferably, trisopropylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, or
10 trisobutylsilyl (meth)acrylate is used in the preparation of the silyl ester copolymer.

The ingredient having biocidal properties for aquatic organisms, which is present in the coating composition according to the present invention, can be a
15 pigment, or a mixture of pigments, having biocidal properties. Examples of suitable biocides are inorganic biocides, e.g. copper oxides, copper thiocyanate, copper bronze, copper carbonate, copper chloride, copper nickel alloys; organometal biocides, e.g. zinc pyrithione (the zinc salt of 2-pyridinethiol-
1-oxide), copper pyrithione, bis (N-cyclohexyl-diazenium dioxy) copper, zinc
20 ethylene-bis(dithiocarbamate) (i.e. zineb), and manganese ethylene-bis(dithiocarbamate) complexed with zinc salt (i.e. mancozeb); and organic biocides, e.g. formaldehyde, dodecylguanidine monohydrochloride, thlabendazole, N-trihalomethylthiophthalimides, trihalomethylthiosulphamides, N-arylmal-
25 imides, 2-methylthio-4-butylamino-6-cyclopropylamino-s-triazine, 3-benzo[b]thien-yl-5,6-dihydro-1,4,2-oxathiazine 4-oxide, 4,5-dichloro-2-(n-octyl)-
3(2H)-isothiazolone, 2,4,5,6-tetrachloroisophthalonitrile, 3-iodo-2-propynylbutyl carbamate, pyridine triphenylborane, a 2-trihalogenomethyl-3-halogeno-4-
cyano pyrrole derivative substituted in position 5 and optionally in position 1,
30 such as 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole, and a furanone, such as 3-butyl-5-(dibromomethylidene)-2(5H)-furanone, and mixtures thereof.

ACO 3010 PDEP

10

In addition to the silyl ester copolymer and the ingredient having biocidal properties for aquatic organisms, the anti-fouling coating compositions according to the present invention optionally comprise another resin or a mixture of other resins, and/or one or more non-biocidal pigments, and/or additives such as one or more thickening or thixotropic agents, one or more wetting agents, fillers, a liquid carrier such as an organic solvent, organic non-solvent or water, etc.

10 Examples of resins that can be used in addition to the silyl ester copolymer in the anti-fouling coating composition according to the present invention include polymers which are free of triorganosilyl ester groups and triorganotin groups but which are reactive in seawater, materials which are slightly soluble or water-sensitive in seawater, and materials which are insoluble in seawater.

15

As examples of suitable polymers that are free of triorganosilyl ester groups and triorganotin groups but which are reactive in seawater, several resins can be mentioned.

For instance, an example of a suitable polymer is an acid-functional film-forming polymer, the acid groups of which are blocked by quaternary ammonium groups or quaternary phosphonium groups. This is for instance described in WO 02/02698.

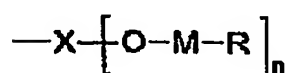
A seawater-reactive polymer can alternatively be a film-forming polymer comprising quaternary ammonium groups and/or quaternary phosphonium groups bound (pendant) to the backbone of the polymer. These quaternary ammonium groups and/or quaternary phosphonium groups are neutralised or, in other words, blocked or capped by counter-ions. Said counter-ions consist of the anionic residue of an acid having an aliphatic, aromatic, or alkaryl hydrocarbon group comprising at least 6 carbon atoms. Such systems are for instance described in EP 02255612.0.

ACO 3010 PDEP

11

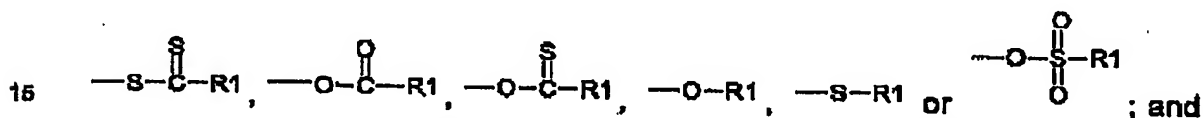
A further example of a suitable seawater-reactive polymer is an acid-functional film-forming polymer the acid groups of which are blocked by groups capable of hydrolysing or dissociating to leave a polymer soluble in seawater, the blocking groups being selected from divalent metal atoms bonded to a monovalent organic residue, divalent metal atoms bonded to a hydroxyl residue, and monoamine groups which form an organic solvent-soluble amine salt of the polymer, as described in WO 00/43460.

For instance, such a seawater-reactive acid-functional film-forming polymer the acid groups of which are blocked, may be a polymer having at least one side chain bearing at least one terminal group of the formula:



wherein X represents $-\overset{\text{O}}{\parallel}{C}-$, $-\overset{\text{S}}{\parallel}{C}-$, $-\overset{\text{O}}{\parallel}{P}-$ or $-\overset{\text{O}}{\parallel}{P}-$

M is a metal selected from zinc, copper and tellurium; x is an integer of 1 to 2; R represents an organic residue selected from



R₁ is a monovalent organic residue, as described in EP-A-204456.

Such a hydrolysable polymer preferably is an acrylic polymer wherein X represents



The parent acrylic polymer having a -COOH group instead of -X-[O-M-R]_n preferably has an acid value of 25-350 mg KOH/g. Most preferably, the hydrolysable polymer has a copper content of 0.3-20% by weight and R₁ is the residue of a high boiling organic monobasic acid. Such hydrolysable polymers can be prepared by the processes disclosed in EP 0 204 456 and EP 0 342 276. The copper-containing film-forming polymer preferably is a copolymer comprising an acrylic or methacrylic ester the alcohol residue of which includes a bulky hydrocarbon

ACO 3010 PDEP

12

radical or a soft segment, for example a branched alkyl ester having 4 or more carbon atoms or a cycloalkyl ester having 6 or more atoms, a polyalkylene glycol monoacrylate or monomethacrylate optionally having a terminal alkyl ether group or an adduct of 2-hydroxyethyl acrylate or methacrylate with caprolactone, as described in EP 0 779 304.

Alternatively, such a seawater-reactive acid-functional film-forming polymer the acid groups of which are blocked, may be a carboxylic acid-functional polymer. For example, it may be a copolymer of acrylic or methacrylic acid with one or more alkyl acrylates or methacrylates, at least some of the acid groups of which have been converted to groups of the formula $-\text{COO-M-OH}$, wherein M is a divalent metal such as copper, zinc, calcium, magnesium or iron, as described in GB 2,311,070.

Another example of such a seawater-reactive acid-functional film-forming polymer the acid groups of which are blocked, is a polymer that is a salt of an amine. Preferably it is a salt of an amine containing at least one aliphatic hydrocarbon group having 8 to 25 carbon atoms and an acid-functional film-forming polymer as described in EP 0 529 693, the acid-functional polymer preferably being an addition copolymer of an olefinically unsaturated carboxylic acid, sulphonic acid, acid sulphate ester, phosphonic acid or acid phosphate ester and at least one olefinically unsaturated co-monomer, the unsaturated carboxylic acid for example being acrylic or methacrylic acid, the unsaturated sulphonic acid for example being 2-acrylamido-2-methylpropane sulphonic acid (AMPS), and the film-forming polymer preferably being an amine sulphonate copolymer containing units of an organocyclic ester as described in WO 99/37723.

As examples of suitable polymers or resins that are slightly soluble or water-sensitive in seawater the following compounds can be mentioned: polyvinyl methyl ether, polyvinyl ethyl ether, alkyd resins, modified alkyd resins, polyurethanes, saturated polyester resins, poly-N-vinyl pyrrolidones, and rosin material.

ACO 3010 PDEP

13

Such a rosin material preferably is rosin, particularly wood rosin or alternatively tall rosin or gum rosin. The main chemical constituent of rosin is abietic acid. The rosin can be any of the grades sold commercially, preferably that sold as WW (water white) rosin. The rosin material can alternatively be a rosin derivative, for example a maleinised or fumarised rosin, hydrogenated rosin, formylated rosin or polymerised rosin, or a rosin metal salt such as calcium, magnesium, copper or zinc rosinate.

As examples of suitable polymers or resins that are insoluble in seawater, the following compounds can be mentioned: modified alkyd resins, epoxy polymers, epoxy esters, epoxy urethanes, polyurethanes, linseed oil, castor oil, soy bean oil, and derivatives of such oils.

Other examples of suitable seawater insoluble polymers or resins are: vinyl ether polymer, for example a poly(vinyl alkyl ether), such as polyvinyl isobutyl ether, or a copolymer of a vinyl alkyl ether with vinyl acetate or vinyl chloride, an acrylate ester polymer such as a homopolymer or copolymer of one or more alkyl acrylates or methacrylates which preferably contain 1 to 6 carbon atoms in the alkyl group and may contain a co-monomer such as acrylonitrile or styrene, and a vinyl acetate polymer such as polyvinyl acetate or a vinyl acetate vinyl chloride copolymer.

Alternatively, the seawater-insoluble polymer or resins can be a polyamine, particularly a polyamide having a plasticising effect such as a polyamide of a fatty acid dimer or the polyamide sold under the Trademark "Santiciser".

If in addition to the silyl ester copolymer, and the ingredient having biocidal properties for aquatic organisms, the coating composition comprises another resin or a mixture of other resins, these other resin(s) can form up to 99 percent by weight of the total amount of resins in the coating composition.

Preferably, the other resin is rosin material and forms up to 20 percent of the total resins in the coating composition to obtain a self-polishing coating of high quality. Alternatively, preferably the other resin is a rosin material and forms 50

ACO 3010 PDEP

14

to 80 percent of the total resins in the coating composition to obtain a so-called controlled depletion coating or a hybrid coating.

In another embodiment, the other resin is a mixture of a rosin material and a seawater-insoluble resin. In that case the rosin material forms 20 up to 80 or
5 95% by weight of the total amount of resins in the coating composition. The rosin material preferably forms at least 25%, more preferably at least 50%, most preferably at least 55% by weight of the total amount of resins in the coating composition. The silyl ester preferably forms at least 30, most preferably at least 50, up to 80 or 90% by weight of the total weight of non-rosin
10 resins, the seawater-insoluble resin being the remainder.

Examples of non-biocidal pigments that can be added to a composition comprising the silyl ester copolymer and the ingredient having biocidal properties for aquatic organisms, are slightly seawater-soluble non-biocides
15 such as zinc oxide and barium sulphate; and seawater-insoluble non-biocides such as fillers and colouring pigments, e.g., titanium dioxide, ferric oxide, phthalocyanine compounds, and azo pigments.

Examples of additives that can be added to a composition comprising the silyl
20 ester copolymer and the ingredient having biocidal properties for aquatic organisms, are reinforcing agents, stabilisers, thixotropes or thickening agents, plasticisers, and liquid carriers.

Examples of suitable reinforcing agents are fibres, e.g., carbide fibres, silicon-containing fibres, metal fibres, carbon fibres, sulphide fibres, phosphate fibres,
25 polyamide fibres, aromatic polyhydrazide fibres, aromatic polyester fibres, cellulose fibres, rubber fibres, acrylic fibres, polyvinylchloride fibres, and polyethylene fibres. Preferably, the fibres have an average length of 25 to 2000 microns and an average thickness of 1 to 50 microns with a ratio between the average length and the average thickness of at least 5.

30 Examples of suitable stabiliser agents are moisture scavengers, zeolites, aliphatic or aromatic amines such as dehydroabietylamine, tetra-ethylorthosilicate, and triethylorthoformate.

ACO 3010 PDEP

15

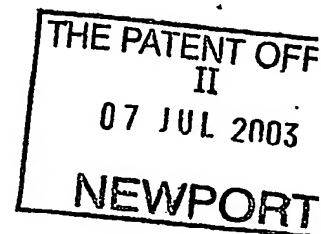
Examples of suitable thixotropes or thickening agents are silicas, bentones, and polyamide waxes.

Examples of suitable plasticisers are phthalate esters such as dibutyl phthalate, butyl benzyl phthalate or dioctyl phthalate, phosphate triesters such as tricresyl
5 or tris(isopropyl)phenyl phosphate, or chlorinated paraffins, and sulphonamides such as N-substituted toluenesulphonamide.

Examples of suitable liquid carriers are organic solvents, organic non-solvents, and water. Suitable examples of organic solvents are an aromatic hydrocarbon such as xylene, toluene or trimethylbenzene, an alcohol such as n-butanol, an
10 ether alcohol such as butoxyethanol or methoxypropanol, an ester such as butyl acetate or isoamyl acetate, an ether-ester such as ethoxyethyl acetate or methoxypropyl acetate, a ketone such as methyl isobutyl ketone or methyl isoamyl ketone, an aliphatic hydrocarbon such as white spirit, or a mixture of two or more of these solvents. It is possible to disperse the coating in an
15 organic non-solvent for the film forming components in the coating composition. The coating can alternatively be water-based; for example it can be based on an aqueous dispersion.

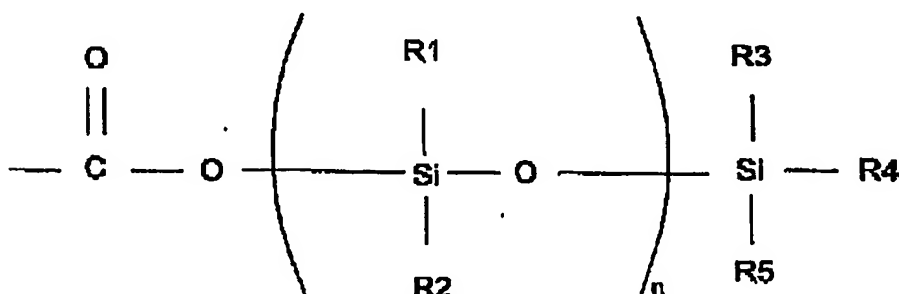
ACO 3010 PDEP

16



Claims

1. Silyl ester copolymer solution having a solid content of at least 55 weight percent and a viscosity of less than 20 poise at 25 °C, comprising a silyl ester copolymer having a weight average molecular weight of less than 20,000.
2. Silyl ester copolymer solution according to claim 1, characterised in that the silyl ester copolymer is a silyl ester copolymer having a weight average molecular weight of less than 20,000, a polydispersity of less than 3.0, a glass transition temperature below 90 °C, less than 70 weight percent of said silyl ester copolymer consisting of side chains having a silyl ester functionality.
3. Silyl ester copolymer solution according to claim 1 or 2, characterised in that the silyl ester copolymer is a copolymer comprising at least one side chain bearing at least one terminal group of the formula:

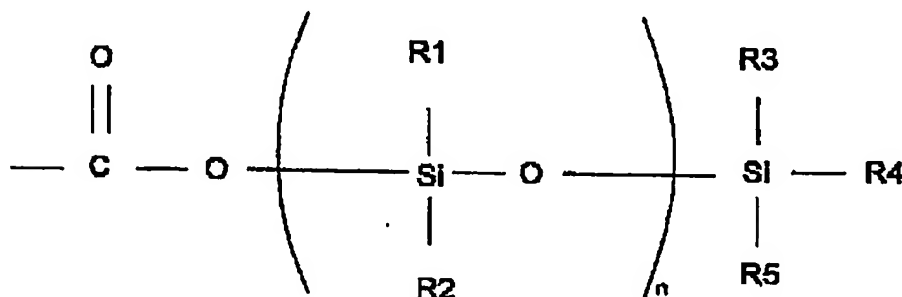


wherein n is 0 or an integer of 1 to 50, and R1, R2, R3, R4, and R5 are each independently selected from the group consisting of optionally substituted C₁₋₂₀-alkyl, optionally substituted C₁₋₂₀-alkoxy, optionally substituted aryl, and optionally substituted aryloxy.

ACO 3010 PDEP

17

4. Silyl ester copolymer solution according to claim 3, characterised in that $n = 0$ and R_3 , R_4 , and R_5 are the same or different and represent methyl, isopropyl, *n*-butyl, or isobutyl.
5. Anti-fouling coating composition having a VOC below 400 gram per litre and a viscosity of less than 20 poise at 25 °C comprising a silyl ester copolymer, and an ingredient having biocidal properties for aquatic organisms.
6. Anti-fouling coating composition according to claim 5, characterised in that the silyl ester copolymer is a silyl ester copolymer having a weight average molecular weight less than 20,000, a polydispersity of less than 3.0, a glass transition temperature below 90 °C, less than 70 weight percent of said silyl ester copolymer consisting of side chains having a silyl ester functionality.
7. Anti-fouling coating composition according to claim 5 or 6, characterised in that the silyl ester copolymer is a copolymer comprising at least one side chain bearing at least one terminal group of the formula:



wherein n is 0 or an integer of 1 to 50, and R_1 , R_2 , R_3 , R_4 , and R_5 are each independently selected from the group consisting of optionally substituted C_{1-20} -alkyl, optionally substituted C_{1-20} -alkoxy, optionally substituted aryl, and optionally substituted aryloxy.

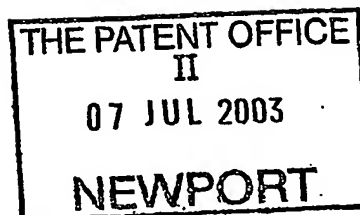
ACO 3010 PDEP

18

8. Anti-fouling coating composition according to claim 7, characterised in that $n = 0$ and $R3$, $R4$, and $R5$ are the same or different and represent methyl, Isopropyl, n-butyl, or Isobutyl.
- 5
9. Anti-fouling coating composition according to any one of claims 5 to 8, characterised in that the composition further comprises one or more polymers or resins selected from the group consisting of compounds which are free of triorganosilyl ester groups and triorganotin groups but
10 which are reactive in seawater, materials which are slightly soluble or water-sensitive in seawater, and materials which are insoluble in seawater.
10. Anti-fouling coating composition according to claim 9, characterised in
15 that the composition comprises a rosin material as a material that is slightly soluble or water-sensitive in seawater.
11. Anti-fouling coating composition according to any one of claims 5 to 10,
20 characterised in that the composition further comprises one or more polymers or resins selected from the group consisting of compounds which are free of triorganosilyl ester groups and triorganotin groups but which are reactive in seawater, materials which are slightly soluble or water-sensitive in seawater, and materials which are insoluble in seawater.
- 25
12. Substrate or structure coated with an anti-fouling coating composition according to any one of claims 5 to 11.

ACO 3010 PDEP

19

**Abstract**

The invention relates to a silyl ester copolymer solution having a solid content of at least 55 weight percent and a viscosity of less than 20 poise at 25 °C, comprising a silyl ester copolymer having a weight average molecular weight of less than 20,000. The invention further relates to coating compositions comprising a silyl ester copolymer, and substrates and structures having a cured coating prepared from such a coating composition.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.